UNISENSE

HYDROGEN SENSOR USER MANUAL

Hydrogen sensor user manual

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UNISENSE A/S

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WARRANTY AND LIABILITY

Notice to Purchaser

This product is for research use only. Not for use in human diagnostic or therapeutic procedures.

Warning

Microsensors have very pointed tips and must be handled with care to avoid personal injury and only by trained personnel.
Unisense A/S recommends users to attend instruction courses to ensure proper use of the products.

Warranty and Liability

The Hydrogen sensor is covered by a 90 days limited warranty. Microsensors are a consumable. Unisense will only replace dysfunctional sensors if they have been tested according with the instructions in the manual within 14 days of receipt of the sensor(s). The warranty does not include repair or replacement necessitated by accident, neglect, misuse, unauthorized repair, or modification of the product. In no event will Unisense A/S be liable for any direct, indirect, consequential or incidental damages, including lost profits, or for any claim by any third party, arising out of the use, the results of use, or the inability to use this product.

Unisense mechanical and electronic laboratory instruments must only be used under normal laboratory conditions in a dry and clean environment. Unisense assumes no liability for damages on laboratory instruments due to unintended field use or exposure to dust, humidity or corrosive environments.

Repair or Adjustment

Sensors and electrodes cannot be repaired. Equipment that is not covered by the warranty will, if possible, be repaired by Unisense A/S with appropriate charges paid by the customer. In case of return of equipment please contact us for return authorization.
For further information please see the document General Terms of Sale and Delivery of Unisense A/S as well as the manuals for the respective products.

CONGRATULATIONS WITH YOUR NEW PRODUCT!

Support, ordering, and contact information

The Hydrogen microsensor is a miniturized sensor for measuring partial pressure of H_2 in the micromolar range.

If you wish to order additional products or if you encounter any problems and need scientific/technical assistance, please do not hesitate to contact our sales and support team. We will respond to your inquiry within one working day.

E-mail: sales@unisense.com

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Further documentation and support is available at our website www.unisense.com.

REPLACEMENT OF SENSORS

Unisense will replace sensors that have been damaged during shipment provided that:

- *The sensors were tested immediately upon receipt in accordance with the delivery note and the manual*
- *The seal is still intact.*
- *The sensors are returned to Unisense for inspection within two weeks.*
- *The sensors are correctly packed for return to Unisense, in accordance with the note included in the sensor box.*

RECOMMENDED AMPLIFIERS

One-channel amplifier: Microsensor Monometer
Multi-channel amplifiers: Microsensor Multimeter

OVERVIEW

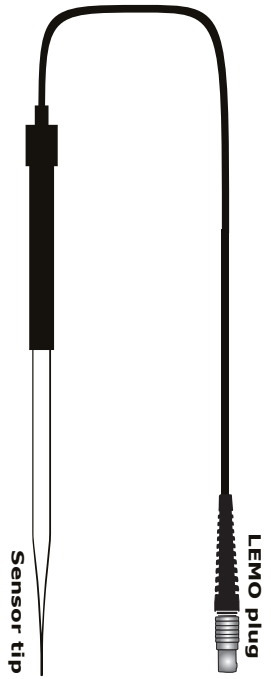
The Unisense hydrogen microsensor is designed for research applications within physiology, biotechnology, environmental sciences, and related areas.

With the minute tip size, excellent response time, and good sensitivity the Unisense hydrogen sensor facilitates reliable and fast measurements with a high spatial resolution.

The Unisense hydrogen microsensor is a miniaturized Clark-type hydrogen sensor with an internal reference electrode and a sensing anode. The sensor must be connected to a high-sensitivity picoammeter where the anode is polarized against the internal reference. Driven by the external partial pressure, hydrogen from the environment will pass through the sensor tip membrane and will be oxidized at the platinum anode surface. The picoammeter converts the resulting oxidation current to a signal.

IMPORTANT

Unisense sensors are neither intended nor approved for use in humans



Schematic view of a hydrogen sensor with a LEMO plug.

THIS MANUAL COVERS THE UNISENSE HYDROGEN MICROSENSORS

$H_2$10 (tip diameter <20 µm)
$H_2$25 (tip diameter 20-30µm)
$H_2$50 (tip diameter 40-60µm)
$H_2$100 (tip diameter 90-110µm)
$H_2$500 (tip diameter ~500µm)
H_2-MR (for use with microrespiration chambers MR-Ch)
H_2-N (Needle type sensor)
H_2-spec - Customer specified.

GETTING STARTED

Unpacking a new sensor

When receiving a new microsensor remove the shock-absorbing grey plastic net.

WARNING

Do not remove the seal and protective plastic tube before these steps and calibration are succesfully completed.

Polarization

The signal from the hydrogen sensor is generated in picoampere. Therefore the hydrogen sensor must be connected to a polarizing picoammeter (e.g. a Microsensor Monometer, a Microsensor Multimeter, or the Unisense PA2000).
Hydrogen sensors should be polarized at +1000 mV. The polarization voltage is set in the amplifier. For details on how to set and check the polarization, consult the user manual of the picoammeter to be used. If you are using a PA2000 amplifier, please check the polarization voltage before connecting the sensor, since incorrect polarization may destroy the sensor.

WARNING

Incorrect polarization may destroy the sensor

Connecting the microsensor

Connect the LEMO connector to the input terminal. The LEMO connector contains connections for both internal reference electrode and sensing anode.

Pre-polarization

Just after connecting the sensor, the signal will be very high and unstable then drop rapidly over the first few minutes. After that the signal will drop slowly for up to 1 hour. Therefore, a period of polarization is necessary before you can use the sensor. This is called the pre-polarization period.
The signal should stabilize at 0-50 picoampere (on the PA2000, the sign will be negative since sensor is positively polarized) for zero hydrogen concentration, depending on the specific sensor. If the sensor is new or has not been operated for several days, it

must be polarized for at least 1 hour before it can be calibrated and used. After shorter periods without polarization, the sensor should be polarized until it has exhibited a stable signal for 10 minutes.
The signal depends on the specific sensor (see the value in the specifications that came with the sensor).
If the signal does not stabilize or is too high or too low, refer to the 'Trouble-shooting' section of this manual.

IMPORTANT
Hydrogen sensors are sensitive to temperature and salinity.

Calibration

Calibration must be performed after the sensor signal has stabilized during pre-polarization.

Zero hydrogen reading

Place/keep the sensor tip in water and read the signal. This signal is your calibration value for zero hydrogen conditions.

Hydrogen reading

The hydrogen sensor responds linearly, and consequently, a two-point calibration is sufficient. Prepare a water phase with a defined hydrogen concentration, which is slightly above the maximum expected hydrogen to be measured. A defined hydrogen concentration can be obtained by 2 different procedures:

1. Use a gas mixture controller to obtain a defined mixture of hydrogen and hydrogen-free inert gas from a gas tank (e.g. N_2) as bulk carrier gas. For instance, to obtain a hydrogen concentration of 10 µM in the calibration chamber at 20°C, bubble the water in the calibration chamber vigorously with a gas mixture containing 98,77 % N_2 and 1,23 % (hydrogen partial pressure 0.0123 atm ´ solubility 813 µmol/liter/atm = 10 µmol/liter – see Table 1). For a Unisense 250 ml calibration chamber, 5 minutes of bubbling at a rate of 5 l per minute is sufficient time to achieve 99% of the concentration. If the

IMPORTANT
Calibration must be performed after pre-polarization when the sensor signal has stabilized. Always use a calibration solution with the same temperature and salinity as the sample solution.

equipment (gas mixture controller) is available, this method can be convenient, as you can switch between different constant hydrogen conditions without changing the water. Use the solubility table (Table 1) to find the correct mixture at temperatures other than 20°C. To obtain correct concentrations, the headspace above the water in the calibration chamber must be closed except for a hole only slightly larger than the microsensor shaft. This effectively prevents ambient air from entering the vessel. We recommend the Unisense Calibration Chamber for calibrations.

2. Add a defined volume of hydrogen-saturated water to a defined volume of water in a calibration chamber. For instance, 1 ml of H_2 saturated water contains 0,805 µmol at 20°C (see Table 1), and to obtain water with a hydrogen concentration of 10 µM, 3.08 ml hydrogen-saturated water should be added to a total volume of 246,9 ml hydrogen free water in the calibration chamber. After the addition of hydrogen-saturated water to the calibration chamber mix it thoroughly by moving the sensor in its protection tube up and down for a few seconds and read the signal when it is stable. Do not stir bubbles into the water or mix by bubbling, as this will remove hydrogen from the water. A magnetic stirrer is not recommended as a mixing tool as a magnetic stirring can introduce electrical noise to the signal. The hydrogen in the water will slowly escape to the atmosphere

Calibration chamber CAL300

WARNING

Vigorous bubbling water with any gas may cause the water to cool considerably. Monitor the temperature to find a suitable bubbling rate, which does not cool the water significantly.

and the concentration can only be
considered constant for a few minutes.

Hydrogen sensors respond linearly in the range of 0 to 100% hydrogen and signals can be linearly converted to partial pressure.

Check and repeat calibration at appropriate intervals to ensure that all measurements can be calibrated to correct concentrations. When the sensor is new, the appropriate interval may be every 30 minutes; later it may be 24 hours. To minimize the need for calibrations, keep the sensor polarized between measurements, unless the time between measurements exceeds several days or unless the picoammeter batteries are running out. The membrane permeability of hydrogen microsensors changes with time, so a change in signal of up to 50% may occur over months.

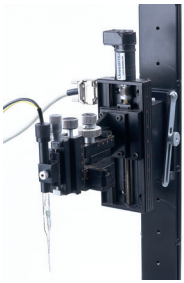
If the sensor functions according to the above procedure, the seal and protective plastic tube can be carefully removed before making measurements.

MEASUREMENTS

Hydrogen sensors can be used for a wide variety of measurements (see our web page for further information www.unisense.com). The most common use of hydrogen sensors is for making profiles in e.g. sediment or animal tissue where a high spatial resolution is wanted, or for hydrogen measurements in water samples.

Mounting of the sensors

Although the Unisense microsensors are made of glass, the tip is flexible and can bend slightly around physical obstacles. The sensor is thus rather sturdy in the longitudinal direction. However, large obstacles like stones or lateral movements of the sensor when the tip is in contact with a solid substrate may cause the tip to break.
Furthermore, due to the small size of the microsensor tip and to the steepness of gradients in many environments, even a displacement of the sensor tip of few microns may change its environment.
Therefore, we recommend that measurements should be performed only in a stabilized set-up free of moving or vibrating devices. We recommend the Unisense lab stand LS18 and the Unisense micromanipulator MM33 (MM33-2 or MMS) for laboratory use. For in-situ use, we recommend our in situ stand (IS19) and a micromanipulator.



Micromanipulator

Electrical noise

The signal of the microsensor is very small (10^{-13} to 10^{-10} ampere). Although both the Unisense picoammeters and the Unisense Hydrogen microsensors are very resistant to electrical noise from the environment, electrical fields may interfere with the sensor signal. Therefore we recommend that unnecessary electrical/mechanical equipment is switched off and the sensor or wires are not touched during measurements and signal recording.

Interference

The presence of sulphide gas can affect measurements. The sensitivity to sulfide gas can be as much as 10 % of the hydrogen sensitivity. In addition exposure to high sulfide gas concentration can affect the calibration of the hydrogen sensor. Therefore measurements done in environments with high sulfide concentrations are not recommended.

ADVANCED USE

Unisense can construct hydrogen sensors for customer requested applications at additional costs. The most frequently requested construction options are described at our web page.

The options include for instance customer specified dimensions, response time, stirring sensitivity, pressure tolerance, range and detection limit. If your specifications for a special hydrogen sensor is not described at our web page please contact sales@unisense.com for further options and prices.

Examples of advanced applications

- Consumption/production rates of hydrogen. E.g. during enzyme assays in small samples in Unisense microrespiration chambers MRCh
- Measurements of hydrogen under high external pressure e.g. in closed pressurized systems, underwater and deep sea applications
- Long-term hydrogen monitoring

If you have questions , please contact sales@unisense.com

STORAGE AND MAINTENANCE

Store the sensor in the protective plastic tube used for shipping.

The hydrogen microsensor can be stored with the tip exposed to water or air. The room in which the hydrogen microsensor is stored should be dry and not too hot (10-30°C). If the sensor is used regularly it can be stored polarized.

Cleaning the sensor

Depending on which substance is present on the sensor tip or membrane, the sensor can be cleaned with different solutes. The standard method is to rinse with 96% ethanol (**NOT in the protection tube**), then rinse with 0.01 M HCl and rinse with water. This will remove most substances.
Alternatively it is possible to rinse with 0.1M NaOH, isopropanol or different detergent

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TROUBLE SHOOTING

Problem	Decreasing sensitivity.
Possible cause	Contamination of the anode surface (e.g. by sulfide).
Solution	Switch the polarization to -1000 mV for 30 seconds. After this period, switch the polarization back to +1000 mV. Repeat calibration procedures when the signal is stable again.

Problem	High and drifting signal.
Possible cause	The sensor tip is broken.
Solution	Replace the hydrogen microsensor.

Problem	The signal is very low.
Possible cause	Loss of the platinum tip due to excessive vibrations.
Solution	Replace the hydrogen microsensor.

Problem	Slow response.
Possible cause	Insoluble compounds deposited at the sensor tip.
Solution	Rinse with 96% ethanol, rinse with 0.01 M HCl and rinse with water.

TROUBLE SHOOTING

Problem	Slow response
Possible cause	The sensor might have lost hydrogen sensitivity temporarily.
Solution	Expose the sensor to high partial pressures of hydrogen > 10 % atm for at least 10 minutes to reactivate the sensor.

Problem	Unstable signal or the signal fluctuates if the set-up is touched or equipment is being introduced in the medium you are measuring in.
Possible cause	Electrical disturbance of the sensor through the tip membrane.
Solution	Ground the set-up using the blue grounding cable supplied with the picoammeter. Connect the reference plug on the picoammeter (blue plug) with the medium you are measuring in.

If you encounter other problems and need scientific/technical assistance, please contact sales@unisense.com for online support (we will answer you within one workday)

Table 1. Equilibrium hydrogen concentrations (µmol/litre) at ambient hydrogen partial pressure of 1 atm. in water as a function of temperature.
Ref. Wiesenburg and Guinasso 1979. J.Chem Eng. Data 24(4):356-360

	Salinity (parts per thousand)									
Temp. °C	0	10	20	30	32	34	36	38	40
-2			901,34	851,79	841,96	832,59	823,21	813,84	804,46
-1			890,18	841,52	832,14	822,77	813,84	804,46	795,54
0	982,59	929,46	879,46	832,14	822,77	813,84	804,46	795,98	787,05
1	969,64	917,86	869,20	822,77	813,84	804,91	795,98	787,50	778,57
2	957,59	907,14	858,93	813,84	804,91	796,43	787,50	779,02	770,98
3	945,54	896,43	849,55	805,36	796,43	787,95	779,91	771,43	763,39
4	934,38	886,16	840,18	796,88	788,39	780,36	771,88	763,84	755,80
5	923,66	876,34	831,70	789,29	780,80	772,77	764,73	756,70	748,66
6	912,95	866,96	823,21	781,70	773,66	765,63	757,59	749,55	741,96
8	893,30	849,11	807,14	767,41	759,38	751,79	744,20	736,61	729,46
10	875,45	833,04	792,41	754,02	746,43	739,29	731,70	724,55	717,41
12	858,93	817,86	779,02	741,96	734,82	727,68	720,54	713,39	706,70
14	843,75	804,02	766,52	730,80	723,66	716,96	710,27	703,13	696,43
16	829,46	791,52	755,36	720,54	713,84	707,14	700,45	693,75	687,50
18	816,96	779,91	744,64	711,16	704,46	698,21	691,52	685,27	679,02
20	805,36	769,64	735,27	702,68	695,98	689,73	683,48	677,23	671,43
22	794,64	759,82	726,34	694,64	688,39	682,14	676,34	670,09	664,29
24	785,27	751,34	718,75	687,50	681,70	675,45	669,64	663,84	657,59
26	776,79	743,30	711,61	681,25	675,00	669,20	663,39	657,59	651,79
28	768,75	736,16	704,91	675,45	669,64	663,84	658,04	652,23	646,88
30	762,05	729,91	699,55	670,09	664,29	658,48	653,13	647,32	641,96

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